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PROJECT ADMINISTRATION DATA SHEET

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Project No. G-35-657 GTRI/~~GIT~~ DATE 11 / 15 / 84

Project Director: Dr. E. Michael Perdue School/~~Lab~~ Geo. Sciences

Sponsor: Georgia Power Company Environmental Affairs
P. O. Box 4545 Atlanta, GA 30302

Type Agreement: Research Agreement dated 11/5/84

Award Period: From 11/1/84 To 10/31/85 (Performance) N/A (Reports)

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Title: Organic Acids in Forest Soils and Streams

ADMINISTRATIVE DATA OCA Contact R. Dennis Farmer x-4820

1) Sponsor Technical Contact:

Dr. W. R. Woodall, Jr.
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P. O. Box 4545
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2) Sponsor Admin/Contractual Matters:

Defense Priority Rating: _____ Military Security Classification: _____

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Date April 27, 1987

Project No. G-35-657 School/~~Unit~~ Geo. Sci.

Includes Subproject No.(s) N/A

Project Director(s) E. M. Perdue GTRC / ~~GKK~~

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Title Organic Acids in Forest Soils and Streams

Effective Completion Date: 12-31-86 (Performance) 12-31-86 (Reports)

Grant/Contract Closeout Actions Remaining: No Del.

- [ ] None
- [X] Final Invoice or Final Fiscal Report
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G35-651

ORGANIC ACIDS IN FOREST SOILS AND STREAMS

Final Report - February, 1987

Submitted to

Georgia Power Company
Environmental Affairs
P.O. Box 4545
Atlanta, GA 30302

Attention: Dr. W. R. Woodall, Jr.

by

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INTRODUCTION

This project was undertaken after initial conversations with Dr. Wayne Swank at the Coweeta Hydrologic Laboratory (U. S. Forest Service) and Dr. Robert Woodall at Georgia Power Company, both of whom felt that their organizations would support a modest research project on the chemistry of organic acids in the forest soils and streams at the Coweeta Hydrologic Laboratory. This Final Report discusses the resulting research project, the design of which was developed in consultation with Dr. Swank. The field and laboratory studies were conducted by Ms. Sarah J. Shealy, as part of her M.S. degree program at Georgia Tech. Dr. E. Michael Perdue performed the modeling calculations that were used to examine the effects of organic acids on Gran titrations for measurement of strong and weak acidity (and alkalinity) in natural waters.

At the time of writing of this Final Report, some of the experiments that were designated for this project are still underway. Accordingly, there will be some places in the Report where tables of data are incomplete. Likewise, some of the conclusions are necessarily tentative and may be changed when all data have been obtained and analyzed. The extra time that has been needed beyond that originally projected is attributable to two main factors:

1. The isolation and purification of soil humic substances from Coweeta soils has been more difficult than expected.
2. Ms. Shealy accepted a full-time position on campus and has not been able to work full-time on this project.

At such time that remaining data are completely determined, an updated revision of the Final Report will be distributed to Dr. Swank and Dr. Woodall.

EXPERIMENTAL PROCEDURES

Three watersheds in the Coweeta Hydrologic Laboratory at Otto, N. C. were selected for inclusion in this study (Watersheds 1, 2, and 27). Watershed 1 is a previously disturbed watershed that now supports a 30-year old white pine plantation. Watershed 2 is an undisturbed watershed that contains abundant yellow poplar, red hickory, and scarlet oak hardwoods. Watershed 27 is a high-elevation watershed containing mainly white pine, chestnut oak, hickory, and rhododendron. The diversity of these watersheds should maximize the possibility of detecting any differences in their respective extractable soil or stream organic acids.

Field Collection of Soil and Stream Samples

All soil and stream samples were collected in June and August, 1985. Stream samples were collected immediately behind the weir in each watershed, using six acid-rinsed 20-liter polyethylene jerricans (120 L per watershed). After removal of an aliquot for dissolved organic carbon (DOC) measurement, each sample was amended with sodium azide to inhibit bacterial activity during storage of samples prior to organic acid extractions (stored at room temperature).

In each watershed, the following procedure was used to collect soil samples. On a transect that is approximately perpendicular to the stream channel, three sites of significantly different slope were selected: a near-streambank site (low slope), a mid slope site (slope = 15-30 %), and a ridge site (slope = 30-50 %). At each site, 6-9 cores of the soil profile were obtained using a 30-inch steel T-barred soil sampler. Each core was carefully divided into Oa, Upper A, Lower A, and B soil horizon sub-samples. The separated sub-samples from the 6-9 soil cores were subsequently combined (by horizon) to produce four composite soil horizon samples (Oa, A1, A2, B) for

TABLE I. Characteristics of Soil Profiles at Sample Collection Sites

Sample[a]	Depth (cm)	Description
01H-O	0.0 - 1.5	Brown loam with pine needle litter, some white fungus
01H-A1	1.5 - 11.5	Dk.-md.brown loam
01H-A2	11.5 - 41.5	Yellow-brown loam with small % scapolite
01H-B	41.5 -	Yellow-Lt.brown loam
01M-O	0.0 - 2.5	Brown loam with pine needle litter
01M-A1	2.5 - 12.5	Yellow-brown loam with minor pebbles and roots
01M-A2	12.5 - 41.5	Yellow-Lt.brown loam, no roots and few pebbles
01M-B	41.5 -	Lt.red-Lt.brown loam with some pebbles
01L-O	0.0 - 2.5	Brown loam with pine needle litter (1:1 litter:soil)
01L-A1	2.5 - 12.5	Black-Dk.brown clay loam with abundant white fungi
01L-A2	12.5 - 41.5	Dk.brown-Red-brown loam with minor scapolite pebbles
01L-B	41.5 -	Yellow-Red-brown loam with minor pebbles
02H-O	0.0 - 1.0	Oak leave litter mat with mixed black-brown soil
02H-A1	1.0 - 6.0	Brown loam with intertwined root network
02H-A2	6.0 - 40.0	Brown-yellow sandy loam with small % of saprolite gravel. Red-brown inclusions of B horizon
02H-B	40.0 -	Red-brown clay loam
02M-O	0.0 - 2.0	Oak leaves litter mat with mixed black-brown soil
02M-A1	2.0 - 9.0	Moist black-brown soil with mica flakes and small roots
02M-A2	9.0 - 43.0	Brown loam with yellow clay inclusions and mica flakes
02M-B	43.0 -	Yellow-brown loam with saprolite inclusions
02L-O	0.0 - 1.5	Oak leaves litter mat mixed with black-brown soil
02L-A1	1.5 - 6.5	Moist black-dk.brown soil with small roots
02L-A2	6.5 - 40.5	Brown loam with yellow clay, less roots than A1
02L-B	40.5 -	Md.brown loam with saprolite inclusions and more yellow clay than A2.
27H-O	0.0 - 3.5	Black-brown litter (branches and oak leaves) and soil
27H-A1	3.5 - 33.5	Black clay loam with some intertwined roots
27H-A2	33.5 - 43.5	Lt.brown with intermixed black loam
27H-B	43.5 -	Yellow/red brown loam with very weathered scapolite
27M-O	0.0 - 4.5	Black-dk.brown litter (small branches, roots, and oak leaves) and soil
27M-A1	4.5 - 34.5	Black-dk.brown loam
27M-A2	34.5 - 44.5	Black-dk.brown loam, darker than A1
27M-B	44.5 -	Dk.brown, minor yellow loam
27L-O	0.0 - 5.0	Black-dk.brown litter (twigs and oak leaves) and soil
27L-A1	5.0 - 35.0	Black-dk.brown loam with 20% root network
27L-A2	35.0 - 55.0	Brown loam
27L-B	55.0 -	Yellow-brown loam with minor saprolite

[a] First two digits = Watershed No.; Next letter (H,M,L) is elevation within a given watershed (analogous to Ridge, Slope, and Stream sites); Last part of ID (O, A1, A2, B) identifies the soil horizon.

each site in a watershed. This protocol ultimately produced 36 composite soil samples (3 watersheds x 3 sites/watershed x 4 samples/site). A brief description of each soil profile is given in Table I, which also introduces the sample identification scheme that will be used throughout this Report.

Moisture Determination on Soil Samples

Soil moisture percentages were determined on most samples by direct measurement of weight loss upon drying samples to constant weight under vacuum for 14 hours at 85°C. Indirect estimates were obtained from recoveries of free-e-dried products (i.e., water equals [initial sample weight - dried organic acids - dried residue]). Typical comparative results are given in Table II. The direct measurements should be more reliable and will be used to convert other soil parameters to a dry-weight basis. The principal use of the indirect estimates is for detection of sample losses during the extractions.

TABLE II. Moisture Contents of Selected Samples - Method Comparison

Sample	Percent Water (by heating)	Percent Water (by difference)
01H-O	46.0	56
01H-A1	14.4	38
01H-A2	16.1	14
01H-B	15.3	27
01M-O	35.6	53
01M-A1	12.6	36
01M-A2	18.0	14
01M-B	11.3	21
01L-O	47.9	57
01L-A1	49.2	33
01L-A2	24.0	26
01L-B	18.6	21

Isolation and Purification of Stream Organic Acids

Because conventional resin adsorption methods recover only about half of the organic acids in typical stream water, a far more laborious approach was used in this study. Each stream sample was concentrated in vacuo from 120 L to about 3.5 L at 35°C in a rotating evaporator. The concentrated solutions were then acidified to pH 2.0 with concentrated HCl, allowed to stand overnight, and then centrifuged at 37,000 g to remove insoluble particles. The supernatant solution was further roto-evaporated to 200 mL and directly freeze-dried. The freeze-dried stream solid was redissolved in a few mL of deionized water to hopefully remove highly water-soluble salts that might be present. This procedure did not work, so the sample was further cleaned up by continuous washing in an Amicon ultrafiltration cell with 0.0001 M HCl. The membrane (YM2) allows very little color to escape from the sample, but readily allows dissolved inorganic cations, anions, and neutral solutes to escape. Measurements were made on the freeze-dried products of the ultrafiltration cleanup experiments.

Extraction and Purification of Soil Organic Acids

Synthetic Rainfall Extractions. Each soil sample was extracted with a synthetic rainfall solution to obtain a relatively soluble fraction of soil organic acids that hopefully resembles the organic acids that are mobilized during actual rainfall events. For simplicity, a single synthetic rain was used for samples from the three watersheds, even though there are documented differences in rainfall chemistry in the watersheds. The volume-weighted average composition of bulk precipitation in Watershed 2 was simulated by an appropriate mixture of NH_4Cl, $CaSO_4$, $MgSO_4$, NaCl, $Na2SO_4$, $K2CO_3$, $H2SO_4$, HNO_3. The final composition of the synthetic rainfall is given in Table III.

TABLE III. Chemical Composition of Synthetic RainFall (based on Watershed 2)

Constituent	µeq/L
H^+	23.7
Ca^{2+}	9.7
Na^+	7.4
NH_4^+	6.8
Mg^{2+}	3.4
K^+	2.4
SO_4^{2-}	33.1
NO_3^-	10.2
Cl^-	7.7
HCO_3^-	2.4
Total Cations	53.4
Total Anions	53.4

Each soil sample was equilibrated for two hours with synthetic rain. The supernatent solution of water-soluble organic acids could be decanted after centrifugation for two hours at 1500 rpm. The soil sample was then re-treated with successive aliquots of synthetic rain until at least 300 mL of supernatent solution were obtained. All supernatent solutions were filtered through prewashed 0.45 µm Millipore filters and then analyzed for DOC. Because of the anticipated low yields of organic acids from synthetic rainfall extractions, all extracts from a single watershed were combined to produce a composite rainfall extract that contains sufficient organic acids for further chemical characterization (i.e., DOC values were measured for all 36 original samples, but only three composite samples were isolated).

The composite synthetic rainfall extracts were concentrated in vacuo to less than 200 mL using a rotating evaporator at 35°C. The concentrated extracts were freeze-dried, then mixed with a minimal volume of water. The resulting slurries were centrifuged at 1500 r.p.m. for 30 min. to remove simple soluble salts, hopefully leaving most of the organic acids in the undissolved fraction. The undissolved fractions were freeze-dried and used in further characterizations.

Strong Base Extractions. Each soil sample was washed initially with 0.1 M HCl to destroy simple carbonate or sulfate salts that might be present and to extract organically and inorganically complexed metals such as iron and aluminum. Ion chromatographic analysis indicated that the concentration of SO_4^{2-} in the acidic washing solutions was generally below 6.0 μeq/L, which was sufficiently low that anion desalting procedures were omitted in the extraction process. Higher levels of SO_4^{2-} would generate a significant amount of sulfuric acid upon removal of cations, causing the organic matter to be badly dehydrated (charred) in the freeze-drying process.

After being acid-washed, each soil sample was rinsed with deionized water and then extracted with 0.1 M KOH under a $N_2(g)$ atmosphere. Exhaustive repetitive extractions yielded about 500 mL of dark brown solution for each soil sample. As in the case of the stream samples, adsorption on hydrophobic resins was rejected in favor of much more time-consuming methods of isolation of organic acids from these solutions, simply because it was felt that the anticipated loss of up to 50% of the organic acids was not acceptable.

The concentrated alkaline extracts were desalted using Amberlite 50W-X8 cation exchange resin (20-40 mesh, H^+-form). Major losses of organic matter could not be avoided in the highly acidic environment of the cation exchange resin, even though samples were extensively diluted to try to minimize such losses (dilution factor = 19 ± 12). Before and after elution of the dilute soil extracts, a 30 mL aliquot was set aside for subsequent measurements of DOC, and K^+ and Na^+ concentrations. The remaining eluant was concentrated in vacuo to 200-250 mL using a rotating evaporator at 35°C. The desalted concentrates were then freeze-dried to obtain solid products.

The inorganic ash contents (see next section for method) on processed samples indicated that further desalting was required for some samples. The first attempt to lower ash contents was simple re-dissolution in deionized

water, with the expectation that ash would be concentrated in the undissolved residue. Each freeze-dried total sample was re-suspended in a centrifuge tube with deionized H_2O and centrifuged at 1500 r.p.m. for two hours. After several repeated treatments, the undissolved phase and combined washings were separately freeze-dried. In some cases, ash contents were acceptably low after this treatment, but many samples were still too badly contaminated with inorganic matter. Those samples were further treated by continuous washing in an Amicon ultrafiltration cell with 0.0001 M HCl (see previous discussion of this technique). The material that was retained in the ultrafiltration cell was freeze-dried and used in subsequent experiments.

Elemental and Thermogravimetric Analyses

Elemental analyses for C, H, and N were obtained on a Perkin-Elmer Model 240C Elemental Analyzer which was calibrated with acetanilide. Each sample was carefully dried over Drierite in a vacuum dessicator for 24 hours at 60°C prior to analysis to eliminate errors arising from moisture. A typical analysis required about 2 mg of sample.

Thermogravimetric analysis (TGA) was used to determine inorganic ash contents of most of the samples in this study. In a typical TGA analysis, samples were heated from 30-950°C at 30°C/min in an oxidizing atmosphere. Ash contents were computed as the residual percent of sample mass at 900°C, even though a few samples were still losing mass at that temperature.

The first derivatives of the %mass-vs.-temperature TGA curves were also analyzed to gain some insight into the nature of the organic matter in the sample. A few samples exhibited a rapid mass loss in the temperature range where cellulose is reportedly oxidized in TGA analyses. This result is not unexpected, given the ubiquitous occurrence of cellulose in the environment and the non-specificity of the extraction methods used to isolate organic

acids in this study. Most TGA analyses, however, were generally featureless, reflecting the underlying heterogeneity of the samples.

Acid-Base Titrations

The organic acids from all samples were titrated at 25°C with 0.1 M KOH to determine the abundances and acidic strengths of acidic functional groups. Organic acid solutions (500 mg/L) were prepared by dissolving the freeze-dried solid samples in an appropriate volume of water. Some samples did not readily re-dissolve in water, presumably because of their relative hydrophobicities. For such samples, complete dissolution could only be accomplished by addition of a small amount of KOH, followed by addition of an equivalent amount of HCl after the sample completely dissolved. Two or three analyses were performed whenever sufficient quantities of sample were available.

All titrations were conducted using an automated titration system that is controlled by an IBM PC-XT computer. Voltage measurements from an Orion Ross combination electrode were monitored with a Hewlett-Packard 3478A digital multimeter that is interfaced to the computer via a National Instruments GPIB-PC board. Titrant solutions were added from a motor-driven Gilmont digital microburet (2.5 mL capacity), with magnetic stirring of the sample solution during titrant addition. The microburet and the magnetic stirrer were interfaced to the computer via a Data Translation DT2805 data acquisition board (via its digital I/O ports). In a typical experiment, the 500 mg/L solution of organic acids was titrated to pH 11-12 using sufficiently small increments of titrant that at least 50 data points could be obtained. From known added base concentrations (C_B) and measured pH values, the electroneutrality equation can be used to calculate the concentration of organic anions at any point in a titration, provided that pH can be correctly converted into $[H^+]$ and $[OH^-]$ concentrations. Assuming that all organic anions are

singly charged (a convenient, but invalid assumption),

$$\Sigma[A^-] = C_B + [H^+] - [OH^-] \qquad (1)$$

The calculation of $[H^+]$ and $[OH^-]$ requires that the Davies equation or a related equation be used to calculate activity coefficients of H^+ and OH^- at the prevailing ionic strength at each point in a titration. At 25°C, the Davies equation for the i^{th} ionic species is:

$$\text{Ln } \gamma_i = -1.17(Z_i)^2 \left| \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right| \qquad (2)$$

where the ionic strength (I) equals the initial ionic strength (I_0) plus contributions from the organic acids and the base titrant. The ionic strength is approximately given by:

$$I = I_0 + 1/2 \left| C_B + [H^+] + [OH^-] + \Sigma[A^-] \right| \qquad (3)$$

Equations 1 and 3 can be combined to obtain:

$$I = I_0 + C_B + [H^+] \qquad (4)$$

Herein lies the computational problem. In order to calculate $[H^+]$, we need to know I, which is a function of $[H^+]$. An iterative calculation was used in this study:

1. Ignoring activity coefficients, estimate $[H^+]$ to be 10^{-pH}.
2. Use current estimate of $[H^+]$ in Eq. 4 to estimate I.
3. Use current estimate of I to calculate all γ_i values from Eq. 2.
4. Re-calculate $[H^+]$ as $10^{-pH}/\gamma_H$.
5. If $[H^+]$ has changed significantly, repeat steps 2-4.

Using the above method, the original $\{C_B, pH\}$ data pairs were converted into $\{pH, [A^-]\}$ pairs that could be subsequently used to estimate abundances

and acidic strengths of acidic functional groups in the soil and water organic acid samples.

Titration data were analyzed using the FITGAUSS computer program, which implements the Gaussian distribution model of Perdue and coworkers. In that model, the complex assemblage of acidic functional groups is modeled as a continuous distribution of proton binding sites whose relative abundances are normally distributed with respect to their pK_a values. In other words, the acidic functional groups with pK_a values near the mean pK_a (μ) are more abundant than stronger or weaker groups. The acid-base chemistry of a structurally related class of binding sites (e.g., carboxylic acids) can thus be described in a model with only three empirical fitting parameters (the mean pK_a value (μ), the variance of pK_a values (σ^2), and the total concentration of functional groups in the specified class (C). In complex mixtures of oxygen-rich organic acids, it is necessary to consider both carboxylic acids and phenols as potential acidic functional group classes. Thus, the FITGAUSS program optimizes six fitting parameters to describe titration data (μ_1, σ_1, C_1, μ_2, σ_2, and C_2).

RESULTS AND DISCUSSION

This section of the Final Report will present the results of the laboratory studies that were described in the previous section. At the time of preparation of this Report, the stream samples have not been completely characterized, so only soil samples will be discussed. The yields of organic acids from the various soil extractions are presented in Table IV, which includes both the DOC concentrations in various extract solutions and the final yield of isolated organic matter from the alkaline extraction of each sample. The following trends are evident in the data.

1. The DOC values of soil extracts vary with the acidity of the extracting solution in the order 0.1 M KOH >> "Rain" > 0.1 M HCl. This result is expected because the DOC contains abundant carboxylic acids, whose solubilities generally decrease at lower pH.

2. At a given sample site, the DOC values of soil extracts vary with soil horizon in the order O > A1 > A2 > B, regardless of the nature of the extractant solution. This result partially reflects the relative abundances of organic matter in the soil horizons, but it also reflects differences in solubility properties, i.e., B-horizon organic matter is thought to be transported from the O-horizon by percolating waters and adsorbed from solution.

3. At a given sample site, the yields of freeze-dried organic acids from alkaline extracts vary with soil horizon in the order O > A1 > A2 > B. This result is consistent with the prior result.

4. At a given sample site, the percentage losses of organic acids through adsorption at low pH on cation exchange resins are in the order B > A2 > A1 > O. This result is in agreement with the lower mobilities of organic acids in the lower soil horizons. B-horizon organic acids were difficult to extract from the soil and they readily leave the aqueous phase to adsorb on surfaces (e.g., the ion exchange resin).

5. Within a given watershed, there is very little difference in the mobilities and yields of organic acids at Low, Medium, and High elevation sites. It does appear, however, that A1:O yield ratios may get larger at lower elevations within the watershed. This would imply that the lower elevation soils contain a greater pool of readily mobilizable organic acids.

6. In inter-watershed comparisons (by elevation and horizon), the yields of extractable organic acids are in the general order 2 > 27 > 1. Watershed 1 (a 30-year old white pine plantation on a previously disturbed watershed soil) is especially low in extractable organic acids. Differences between the other watersheds are less dramatic.

TABLE IV. The Moisture Contents and Yields of Extractable Organic Acids from Coweeta Soil Samples.

Sample	Percent Water	DOC (mg C per gram dry soil) Acid	Rain	Base	CEX	Yield mg/g	Inorganic Ash (%)
01H-0	46	0.2	4.1	292	69	129	n.a.
01H-A1	14	0.5	0.8	62	12	43	n.a.
01H-A2	16	0.5	<0.1	46	4	23	n.a.
01H-B	15	0.3	<0.1	10	<1	12	n.a.
01M-0	36	0.5	3.1	120	67	161	n.a.
01M-A1	13	0.4	0.2	37	17	57	n.a.
01M-A2	18	0.4	<0.1	18	10	42	n.a.
01M-B	11	0.3	<0.1	5	1	9	n.a.
01L-0	48	0.6	2.6	72	75	107	n.a.
01L-A1	34	0.5	<0.1	96	42	72	n.a.
01L-A2	24	0.5	<0.1	50	14	43	n.a.
01L-B	19	0.2	<0.1	16	2	13	n.a.
02H-0	56	1.3	6.5	163	104	264	10.1
02H-A1	40	0.7	1.5	99	54	147	16.7
02H-A2	20	0.4	<0.1	9	6	29	24.7
02H-B	19	<0.1	<0.1	3	<1	30	35.9
02M-0	69	1.5	10.9	202	78	292	9.6
02M-A1	60	1.1	6.0	143	60	230	18.7
02M-A2	18	0.4	<0.1	21	4	68	44.4
02M-B	17	0.1	<0.1	6	<1	26	43.8
02L-0	68	1.5	7.1	203	86	324	7.2
02L-A1	63	1.0	5.3	206	70	319	8.5
02L-A2	23	0.7	<0.1	27	6	68	27.3
02L-B	22	0.2	<0.1	4	3	36	32.0
27H-0	37	0.3	3.2	82	62	104	n.a.
27H-A1	53	0.5	1.8	132	88	142	n.a.
27H-A2	52	0.8	1.6	88	77	53	n.a.
27H-B	24	0.7	<0.1	19	8	32	n.a.
27M-0	59	1.3	5.8	92	85	242	15.7
27M-A1	44	0.7	0.8	97	48	137	17.2
27M-A2	17	0.2	0.1	43	14	64	19.8
27M-B	48	0.3	<0.1	22	13	86	21.4
27L-0	37	0.7	4.3	104	54	171	36.7
27L-A1	48	0.9	2.9	122	65	176	10.5
27L-A2	36	0.4	0.4	16	16	75	19.4
27L-B	34	0.2	<0.1	20	10	48	22.5

The results of the extended cleanup procedures on ash contents of organic acid extracts are summarized in Table V. The Soluble Mass fraction includes organic matter that was further desalted by ultrafiltration. The purification steps clearly decreased the ash contents of the soluble fraction and increased ash contents in the insoluble residues. In some cases, however, the ash contents of soluble fractions were still quite high.

The ash-corrected elemental compositions of isolated soil organic acids are given in Table VI, along with several commonly used atomic ratios (H/C, N/C, and O/C). Most of the data are well within the range of compositions that is commonly reported for humic substances. Other results may be experimental artifacts. The large amount of missing data in this Table precludes any thorough comparative analysis of compositional data within and between watersheds. It does appear, however, that the organic acids from Watershed 27 are less oxidized than from Watershed 1.

The results of the acid-base titrations are summarized in Table VII as the fitting parameters of the Gaussian distribution model. The mean pK_a value of the stronger acids (carboxylic acids) is about 3.8, and the standard deviation of pK_a values around the mean is about 2.2 log units. These results are comparable to the acidic properties of other soil and aquatic substances (for Satilla River humic substances, $\mu = 3.7$ and $\sigma = 2.5$). The carboxyl contents of these samples average about 7 μeq/mg C, which is somewhat below the values normally reported for humic substances (10-15 μeq/mg C). Because our samples contain non-humic (and possibly non-acidic) organic matter, these results are considered reasonable. Although fitting parameters are tabulated for the weaker acidic functional groups, the results are not thought to be very reliable and will not be interpreted here (we know that HCO_3^- in the titrant caused problems in the high pH end of our titration curves).

TABLE V. Ash Contents and Yields of Water-Soluble and Insoluble Fractions of Extracted Soil Organic Acids.

Sample	Soluble Fraction Mass(g)	Soluble Fraction Ash(%)	Insoluble Fraction Mass(g)	Insoluble Fraction Ash(%)
01H-O	0.02	13.9	0.83	13.9
01H-A1	0.02	n.a.	0.59	36.5
01H-A2	0.09	3.7	2.35(?)	n.a.
01H-B	0.01	29.1	0.14	15.5
01M-O	0.88	6.9	2.50(?)	n.a.
01M-A1	0.33	1.1	0.21	n.a.
01M-A2	0.23	1.2	n.a.	n.a.
01M-B	0.01	24.5	0.88	61.1
01L-O	0.48	3.7	n.a.	n.a.
01L-A1	0.36	1.3	n.a.	n.a.
01L-A2	0.20	6.0	1.46	n.a.
01L-B	n.a.	n.a.	0.23	n.a.
02H-O	0.65	n.a.	0.45	15.4
02H-A1	0.42	8.6	0.43	31.5
02H-A2	0.10	16.8	0.09	41.9
02H-B	0.20	7.2	0.18	65.8
02M-O	0.49	6.8	0.33	15.8
02M-A1	0.42	18.9	0.44	25.5
02M-A2	0.34	n.a.	0.21	72.3
02M-B	0.09	13.9	0.21	61.2
02L-O	0.63	n.a.	0.33	7.5
02L-A1	0.52	n.a.	0.38	15.6
02L-A2	0.26	12.3	0.21	44.5
02L-B	0.10	13.7	0.15	45.0
27H-O	0.50	2.2	n.a.	n.a.
27H-A1	0.45	2.8	1.19	n.a.
27H-A2	0.45	5.2	0.88	n.a.
27H-B	0.12	8.6	n.a.	n.a.
27M-O	0.44	12.0	0.46	0.9
27M-A1	0.33	n.a.	0.38	22.3
27M-A2	0.21	n.a.	0.27	26.9
27M-B	0.16	45.0	0.15	24.2
27L-O	0.97	36.3	0.11	41.8
27L-A1	0.47	0.0	0.37	13.8
27L-A2	0.22	15.4	0.22	26.6
27L-B	0.35	34.2	0.09	34.6

TABLE VI. Elemental Compositions (Dry, Ash-Free Basis) of Extracted Soil Organic Acids.

Sample	%C	%H	%N	%O	H/C	N/C	O/C
01H-0	43.08	6.04	2.26	48.60	1.68	0.04	0.85
01H-A1							
01H-A2	46.78	4.57	1.67	46.98	1.17	0.03	0.75
01H-B	37.50	3.72	1.53	57.25	1.19	0.03	1.15
01M-0	47.22	4.83	2.02	45.93	1.23	0.04	0.73
01M-A1	40.97	3.98	1.70	53.35	1.17	0.04	0.98
01M-A2							
01M-B	40.61	4.61	1.77	53.01	1.36	0.04	0.98
01L-0	47.78	4.77	2.13	45.32	1.20	0.04	0.71
01L-A1	46.48	4.48	2.05	46.99	1.16	0.04	0.76
01L-A2	42.58	4.23	1.83	51.36	1.19	0.04	0.90
01L-B	{ 10.22	0.97	0.35	87.46	1.14	0.03	6.42 }
02H-0							
02H-A1							
02H-A2							
02H-B							
02M-0							
02M-A1							
02M-A2							
02M-B							
02L-0							
02L-A1							
02L-A2							
02L-B							
27H-0	51.37	5.26	2.16	41.22	1.23	0.04	0.60
27H-A1	50.27	4.84	1.79	43.11	1.16	0.03	0.64
27H-A2	50.97	4.69	1.26	43.09	1.10	0.02	0.63
27H-B	39.21	4.46	1.76	54.58	1.36	0.04	1.04
27M-0							
27M-A1							
27M-A2							
27M-B							
27L-0							
27L-A1							
27L-A2							
27L-B							

TABLE VII. Gaussian Distribution Estimates of Concentrations and Acidic Strengths of Soil Organic Acid Functional Groups.

Sample	Conc[1][a]	Mu[1]	Sigma[1]	Conc[2][a]	Mu[2]	Sigma[2]
01H-O						
01H-A1						
01H-A2						
01H-B						
01M-O	3.52	3.98	1.63	3.00	8.90	1.98
01M-A1	7.06	3.82	1.99	5.08	8.98	1.10
01M-A2						
01M-B						
01L-O	7.00	3.76	2.51	2.60	9.06	1.56
01L-A1	7.41	4.18	2.16	4.88	9.19	0.71
01L-A2	10.39	3.81	2.29	8.04	9.31	0.83
01L-B	???	3.55	3.58	???	9.15	1.03
02H-O						
02H-A1						
02H-A2						
02H-B						
02M-O						
02M-A1						
02M-A2						
02M-B						
02L-O						
02L-A1						
02L-A2						
02L-B						
27H-O	6.29	3.88	2.26	3.16	9.03	1.70
27H-A1	6.43	4.18	2.23	2.34	8.92	1.94
27H-A2	6.08	3.80	2.48	2.58	9.08	1.02
27H-B	11.16	3.10	2.48	3.90	9.08	0.75
27M-O						
27M-A1						
27M-A2						
27M-B						
27L-O						
27L-A1						
27L-A2						
27L-B						

[a] [Conc] values in μeq/mg C

The concentrations and strengths of the acidic functional groups in the extracted organic acids from Coweeta soil are sufficient to contribute to the acid-base chemistry of local streams. If these streams contained only DOC, the following pH values and organic anion concentrations would be predicted from the above titration data.

DOC (mg/L)	pH	[Anions, μeq/L]
1	5.27	5.4 (max 7.3)
2	4.99	10.2 (max 14.6)
4	4.72	19.2 (max 29.2)
8	4.45	35.4 (max 58.4)

Of course, Coweeta streams do contain additional solutes, particularly HCO_3^-, so pH values are higher. Consequently, the organic anion concentrations are probably somewhere between the predicted values and the Max. values in the above table. For example, at a DOC of 2 mg/L, the organic anion concentration should fall between 10.2 and 14.6 μeq/L. There is some additional complexity arising from complexation of metal ions by organic matter, but it is beyond the scope of this project.

MODELING GRAN TITRATION ESTIMATES OF STRONG AND WEAK ACIDITY

The electroneutrality equation for a solution containing C_B, C_A, and C_{HA} mole/L of strong base, strong acid, and weak acid is:

$$C_B + [H^+] = C_A + [OH^-] + \alpha C_{HA} \quad (5)$$

where α is the degree of ionization of the weak acid (HA) at pH = -Log$[H^+]$. This equation can be arranged to yield:

$$C_B - C_A = [OH^-] + \alpha C_{HA} - [H^+] \quad (6)$$

If the term $[C_B - C_A]$ equals zero, the pH of the solution is simply that of a pure solution of HA. Negative or positive $[C_B - C_A]$ values indicate solutions that contain excess strong acids and strong bases, respectively. A titration with strong acid or base simple changes the $[C_B - C_A]$ term, causing corresponding changes to occur on the right hand side of Eq. 6. When numerically generating titration data, as was done in these Gran titration simulations, it is far easier to systematically vary the right hand side of Eq. 6 and calculate the $[C_B - C_A]$ term, assuming that the pH dependence of α is known or can be realistically modeled.

In attempting to assess the short-term and long-term effects of acidic deposition on the titration alkalinities and/or acidities of lakes and streams, many authors have attempted to distinguish between "strong" and "weak" acids in natural water samples, the implication being that "strong" acids are a measure of atmospheric inputs of sulfuric and nitric acids. One of the most common analytical methods that is used for this purpose is the Gran function analysis of potentiometric titration data.

At the simplest level, a Gran analysis assumes that, in the absence of weak acidity (C_{HA} = 0), one mole of H^+ will be neutralized for each mole of

added OH^- in an acidity titration (sample is titrated with a strong base to measure its titratable acidity). Therefore, a plot of $[H^+]$ vs. $[C_B - C_A]$ should have a slope of -1 up to the equivalence point of the titration. Beyond that point, the sample contains nothing to react with added base, so one mole of $[OH^-]$ will appear in solution for each mole of added base, and a plot of $[OH^-]$ vs. $[C_B - C_A]$ will have a slope of +1.

When a sample contains weak acids ($C_{HA} > 0$), Gran plots are more complex, but are usually interpreted in much the same fashion. A Gran titration plot for an ideal hypothetical weak acid is given in Figure 1. The Y-axis corresponds to $[H^+]$ at low pH and to $[OH^-]$ at high pH. The difference between the X-axis intercepts of the $[H^+]$ and $[OH^-]$ Gran functions is the Weak Acidity of the sample. More generally, the Strong Acidity of a sample is calculated from the X-axis intercept of the H^+ Gran function, the Total Acidity of the sample is calculated from the X-axis intercept of the OH^- Gran function, and the Weak Acidity is then calculated as the difference between Total and Strong Acidity.

$$\text{Total Acidity} = [OH^- \text{ Gran Intercept}]$$

$$\text{Strong Acidity} = [H^+ \text{ Gran Intercept}]$$

$$\text{Weak Acidity} = \text{Total Acidity} - \text{Strong Acidity}$$

In general, Gran function analysis of titration data for weak acid solutions is not as simple as in the idealized example in Figure 1. The principal complication arises because most common weak acids are appreciably ionized in dilute aqueous solutions, which results in significant non-linearity in Gran functions, especially the $[H^+]$ Gran function. In a typical acidity titration, the water sample is amended with a known amount of strong acid (e.g., HCL) to lower its pH to around pH 3.0 and suppress ionization of weak acids. The resulting solution is then titrated with strong base such as NaOH to high pH.

It is hoped that, after corrections for the initially added HCL, the Gran function analysis will yield better estimates of Strong and Weak Acidity for the original sample.

In the calculations that were done in this study, titration data were numerically generated for solutions containing various concentrations of strong acids, strong bases, and humic substances. Data were generated at 0.1 pH intervals in the pH 3.0-11.0 range. The degree of ionization of the acidic functional groups in the humic substances was calculated at each pH from the average Gaussian distribution model fitting parameters from all samples that have thus far been characterized (Conc[1] = 7.3 μeq/mg C, Mu[1] = 3.8, Sigma[1] = 2.2, Conc[2] = 4.0 μeq/mg C, Mu[2] = 9.1, Sigma[2] = 1.3). The Gran functions for Total Acidity and Strong Acidity were computed using data from pH 3.0-4.0 and from pH 10.0-11.0, respectively. All Gran plots were highly linear ($r^2 > 0.999$) with absolute slopes that were close to one (lowest slope found was 0.95). Some results are summarized in Table VIII.

TABLE VIII. Gran Function Analysis of Coweeta Organic Acid Titration Data

	-------- Actual Composition --------				----- Gran Analysis -----		
DOC (mg/L)	Mineral Acidity	Carboxyl Acidity	Phenolic Acidity	Total Acidity	Strong Acidity	Weak Acidity	Total Acidity
1.0	0.0	7.3	4.0	11.3	3.8	6.4	10.2
2.0	0.0	14.6	8.0	22.6	7.6	12.9	20.5
4.0	0.0	29.2	16.0	45.2	15.3	25.7	41.0
8.0	0.0	58.4	32.0	90.4	30.6	51.4	82.0
16.0	0.0	116.8	64.0	180.8	61.2	102.8	164.0
24.0	0.0	175.2	96.0	271.2	91.7	154.3	246.0
32.0	0.0	233.6	128.0	361.6	122.3	205.7	328.0

The estimated Total Acidities are about 90-91% of the actual Total Acidities in all titrations, with DOC covering the normal range of natural waters. If the two classes of acidic functional groups are classified as carboxylic acids and phenols, as in Table VIII, the underestimation of Total Acidity is due to incomplete titration of the phenols. More importantly,

though, is the Gran analysis of Strong and Weak Acidity. In all titrations, about 37% of the Gran Total Acidity is detected as Strong Acidity. These "samples" contain no strong acids such as H_2SO_4 or HNO_3, so the Strong Acidity is actually part of the organic acidity of the "samples". The Strong Acidity corresponds to about 52% of the carboxylic acid content of the "samples". In other words, a Gran titration analysis will report 52% of the carboxylic acids in Coweeta organic acids as Strong Acidity. It is clearly incorrect to equate Gran Strong Acidity with atmospherically derived mineral acidity.

The same numerical treatment is also applied to alkalinity titrations, in which strong acid (HCl) is added to a sample until the solution pH is below 4.5, the approximate H_2CO_3 equivalence point. Further additions of HCl to a pH of about 3 yields suitable data for a Gran function analysis. The same Gran plot used for Strong Acidity is used for Total Alkalinity. Accordingly, 48% (100-52) of the carboxylic acids of Coweeta organic acids will be protonated during the titration and be included in Gran estimates of Total Alkalinity, which is usually assumed to be due solely to inorganic bases, especially HCO_3^-.

The recent EPA survey of potentially acid-sensitive lakes in the Eastern U.S. included 33 lakes from North Carolina. The average alkalinity (acid-neutralizing capacity) and HCO_3^- concentration for those lakes are 169.4 and 162.4 μeq/L, respectively. Using the average DOC of 1.92 mg/L and the Coweeta organic acids' acidic properties, the organic anion portion of the average ANC is predicted to be [1.92 mg C/L][7.3 μeq/mg C][0.48] = 6.73 μeq/L, which accounts for virtually all of the discrepancy between ANC and $[HCO_3^-]$.

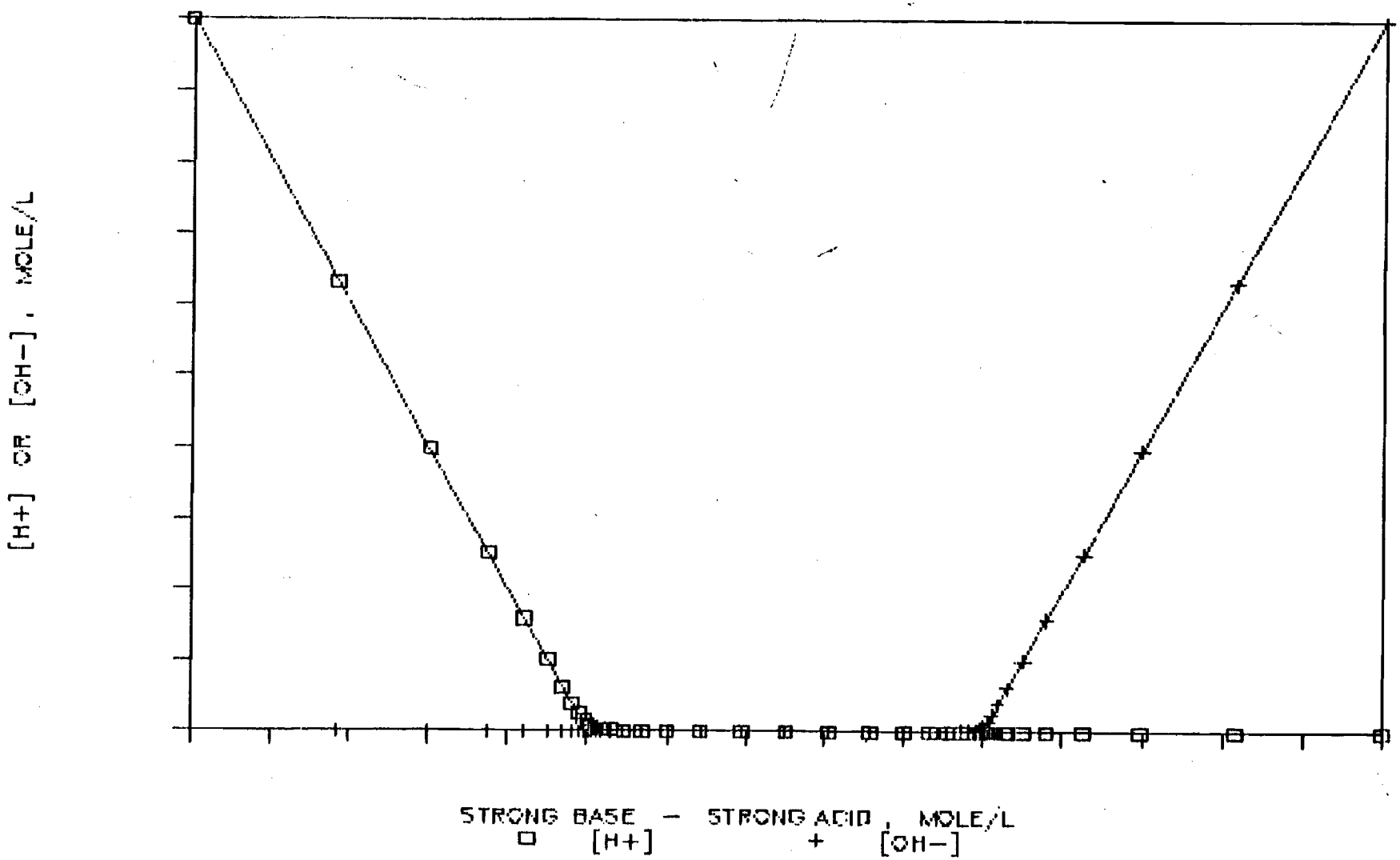
SUMMARY AND CONCLUSIONS

The data that have thus far been obtained in our studies of extractable organic acids in Coweeta watersheds 1, 2, and 27 lead to several tentative conclusions. As more data become available, it is likely that some of those conclusions may have to be modified. For now, though, the following conclusions can be made.

Watershed #1 yields lower quantities of extractable organic matter than the other watersheds. We have no explanation for this observation at this time, but Watershed #1 is a 30-year old white pine plantation and the other watersheds contain predominantly hardwood trees. In any given watershed, O horizon samples yield the largest quantities of extracted organic acids, followed by A1, A2, and B horizon samples. Because of the greater thicknesses of the A1 and A2 horizons, however, the O horizons never account for more than 20 percent of the soil organic acid reservoir. The relative yield of extractable organic acids in the lower horizons is greatest in WS#27, followed by WS#2 and WS#1. There is a clear, expected increase in the yield of extractable organic acids with increasing pH of the extractant (0.1 M KOH >> "Rain" > 0.1 M HCl).

There are only minor differences in the elemental and functional group compositions of organic matter from the three watersheds, with the possible exception that organic matter from WS#27 is less highly oxidized. The acidic strengths of extractable organic acids are quite similar to those of humic substances from surface waters and soils, but the concentrations (μeq/mg C) are lower, indicating the presence of non-humic organic matter in the Coweeta soil extracts. There were no efforts to eliminate such substances in the extractions.

From the titrations of extractable organic acids, numerical modeling of titration data, and Gran analysis of simulated titrations, several other conclusions can be drawn. First, the concentrations and acidic strengths of Coweeta organic acids are such that, in solutions with pH > 4.5, the organic anion content is predicted to fall between 4.4 and 7.3 μeq/mg C. For example, a water sample with a DOC of 2.0 mg/L should have an organic anion concentration of 10-15 μeq/L. The presence of strongly dissociated organic acids confounds the simple Gran analyses that are used to measure solution alkalinities and/or acidities. In the former case, some of the organic anion content is included in the alkalinity. In the latter case, 52% or so of the carboxylic acids in Coweeta organic acids will appear as "strong" acids in a Gran analysis of "strong" and "weak" acidity. The common assumption that only mineral acids such as H_2SO_4 and HNO_3 can account for the presence of "strong" acidity in natural waters is simply wrong.


[H+] OR [OH−], MOLE/L
STRONG BASE − STRONG ACID, MOLE/L
□ [H+]
+ [OH−]